(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 042 678
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 81302434.6

(22) Date of filing: 02.06.81

(51) Int. Cl.³: C 09 D 7/00
C 08 J 3/02, C 09 K 7/00
C 08 L 33/00, C 09 D 5/00

(30) Priority: 13.06.80 GB 8019466

(43) Date of publication of application:
30.12.81 Bulletin 81/52

(84) Designated Contracting States:
BE CH DE FR IT LI NL

(71) Applicant: SCOTT BADER COMPANY LIMITED
Wollaston
Wellingborough, Northamptonshire NN9 7RL(GB)

(72) Inventor: Khan, Zubair Munir
8 Wantage Road
Irchester, Northants NN9 7HE(GB)

(74) Representative: Harrison, David Christopher et al,
MEWBURN ELLIS & CO 70 & 72 Chancery Lane
London WC2A 1AD(GB)

(54) **Method of thickening.**

(57) Aqueous based compositions can be thickened by mixing in a thickener which is a water-in-oil emulsion. Preferably the thickener contains water soluble polyacrylamide or polymethacrylamide homopolymers or copolymers with other suitable monomers. The polymers may be slightly cross-linked. The thickeners are themselves of low viscosity and are easy to handle, but act to thicken aqueous based compositions effectively and quickly, typically dissolving in water in about one minute. They are also resistant to bacterial attack.

They have wide application, examples of compositions which may be thickened are emulsion paints, carpet backing compounds textile pigment printing pastes, drilling mud, latex, and wallpaper paste.

EP 042 678 A1

METHOD OF THICKENING

Thickeners for aqueous based compositions such as paints, adhesives, textile printing pastes, carpet backings, cosmetics, drilling muds, latices etc are usually natural or synthetic products supplied as solids or dilute solutions. Typical examples of natural or modified natural products are starches, carboxymethyl cellulose, hydroxyethyl cellulose etc. and among the synthetic products used are polyvinyl alcohol, sodium polyacrylate gels etc. These materials are often difficult to handle insofar as they are difficult to dissolve and use, they are not very efficient, they are variable in quality and possess other technical disadvantages like being prone to bacterial attack.

We have now discovered that inverse (i.e. water-in-oil) emulsions of water soluble polyacrylamide and polymethacrylamide homopolymers and copolymers of these with acrylic or methacrylic acids, cationic monomers such as dimethylaminoethyl methacrylate quarternised with dimethyl sulphate etc can be empolyed as efficient, easy to use thickener in these systems. The ratios of these monomers can

range from 100/10 (i.e. (meth) acrylamide homopolymer to 10 (methyl) acrylamide/90 comonomer). Minor amounts of other ethylenically unsaturated monomers may be included. Some of these inverse emulsions of high molecular weight, greater than 1×10^6, preferably greater than 6×10^6, have been used as flocculants. In this new use they overcome the well known problems of dissolving solid products which can take several hours since the polymer has always been in the aqueous phase.

In the present invention we have found that by reversing the emulsion (whether by the addition of water or the addition of a reversing surfactant and water) the low viscosity water in oil emulsion is almost instantaneously inverted to an extremely viscous paste of water soluble polymer in the aqueous phase.

Formulations can be provided wherein the water phase of the inverse emulsion includes a reversing surfactant so that addition of pure water will cause reversion to an oil in water emulsion. But otherwise the addition of a water soluble inversion surfactant to either the inverse emulsion or the water causes the water in oil emulsion to

revert and become water soluble and because the emulsion is essentially already in the aqueous phase, rapid solubility occurs. Typically the dissolution in water takes around 1 minute compared to several hours for solid materials.

It is possible to produce lightly crosslinked products of this type by including a small amount, 0.1-5% by weight, of a di- or poly-functional olefinically unsaturated compound such as allyl methacrylate, diallyl phthalate, divinyl benzene, triallyl isocyanurate or methylene bis-acrylamide in the polymer.

These water-in-oil emulsions are of low viscosity 200-800 cps at 25°C (typically 500 cps) and 15-40% solids (typically 25-30%). They can easily be inverted in water based systems to give very high solution viscosities.

The water-in-oil emulsions typically consist of:-

15-40% (typically 25%) polymer solids

2-10% (typically 5%) oil soluble surfactant HLB below 7

13-25% (typically 20%) oil phase usually a hydrocarbon such as white spirit,

plasticiser such as dibutyl phthalate,

50% water.

* (R) = Esso trade name.

Up to 5 p.p.h of an inversion surfactant (usually water soluble) may be incorporated.

Sorbitan mono oleate can be used as an oil-soluble surfactant.

The main advantages of using these water in oil emulsions over other solid and liquid products are their ease of production, ease of handling, rapid solubility, efficiency, freedom from bacterial attack, salt stability and temperature stability coupled with low cost.

The following examples illustrate the use of these inverse emulsions as thickeners.

Example 1

Use in thickening emulsion paints.

In this example, Thickener A is a 25% active water in oil emulsion, containing an inversion surfactant, of an acrylamide/sodium acrylate copolymer crosslinked with 0.5% of allyl methacrylate.

The following paint formulation was used:-

Water - (1)	100	
Thickener (solid)	2.2	
Dispersant (solid)	1.8	
Antifoam	0.9	
Pigments	385.0	(Mixture of titanium dioxide and calcium carbonate)
Binder latex	298.0	
Water	158.0	

The binder latex used was a styrene/butyl acrylate emulsion of 55% solids.

The paints were made by dissolving the thickener in water ((1)) then adding the pigment dispersant and antifoam. The pigments were then dispersed in this mixture using a high speed stirrer. Finally the binder latex and water were added. Two paints were made, one using Thickener A, the other using a conventional hydroxyethyl cellulose thickener.

When Thickener A was used the ease of handling, ease of mixing and ease of dissolution were readily apparent. The rheology of the paints were similar and the viscosity of the paint made from Thickener A was slightly higher.

Using Thickener A, unlike the hydroxyethyl cellulose, paints may be made by omitting the thickener from the dispersion stage and post adding this after the binder latex. This method offers process and quality control advantages.

Example 2

Use in thickening carpet backing compounds.

Thickener B was used in this example and this is a 25% active water in oil emulsion, containing inversion surfactant, of acrylamide/sodium acrylate copolymer crosslinked with 0.25% of diallyl phthalate.

Two carpet backing compounds were made. These consisted of thickener styrene/butadiene latex, filler, dispersing agent for filling and antifoam. One mixture was made using Thickener B and the other using the same amount (on a solids basis) of a conventional acrylic emulsion thickener.

The use of Thickener B produced a compound having a viscosity 20% higher than the conventional product indicating a lower amount may be used to achieve a given viscosity.

Example 3

Use in thickening textile pigment printing pastes.

In this example Thickener C was used. This is a 25% active water in oil emulsion, containing inversion surfactant, of acrylamide/ammonium acrylate copolymer crosslinked with 0.50% of allyl methacrylate. This product was compared to a well known commercial product based on an ethylene/maleic anhydride polymer in dry powder form.

The Thickener C produced pastes which thicken in one minute compared to the lengthy time for the conventional product. In addition, unlike the conventional product, the addition of ammonia was not necessary.

Printing performacne was similar.

Example 4

Use in thickening Drilling Muds for oil recovery.

In this example, Thickener D was used. This is a 25% active water in oil emulsion of an acrylamide/sodium acrylate copolymer. (No inversion surfactant is necessary in this example).

Two typical sea water based bentonite muds were made up one using Thickener D and the other using an equivalent amount of a conventional solid, high molecular

weight carboxymethyl cellulose (CMC). The formulation based on Thickener D showed a higher viscosity, a higher yield point and lower fluid loss in addition to a much shorter dissolving/mixing time.

Example 5

Use in latex thickening.

In this example, Thickener E was used. This is a 25% active water in oil emulsion, containing an inversion surfactant, of an acrylamide/sodium acrylate copolymer crosslinked with 3% divinyl benzene.

Natural rubber latex was thickened using Thickener E and separately an equivalent amount of a conventional sodium polyacrylate gel thickener. The Thickener E was much easier to handle than the gel and exhibited greater thickening efficiency.

Example 6

Use in thickening water for a wallpaper paste.

In this example Thickener F was used. This is a 25% active water in oil emulsion containing an inversion surfactant of an acrylamide/sodium acrylate copolymer crosslinked with 0.1% of allyl methacrylate.

Water was thickened by stirring in 3% of Thickener F and in comparison an equivalent amount of conventional dry starch paste. The materials produced similar viscosities but the Thickener F dissolved in 1 minute compared to 15 minutes for the starch. The thickened adhesive showed good open time, grab slip etc. and did not suffer from bacterial attack.

CLAIMS:

1. A method of thickening an aqueous based composition by mixing the composition with a thickener characterised in that the thickener is a water-in-oil emulsion.

2. A method according to Claim 1 in which the water phase of the emulsion contains water soluble polyacrylamide or polymethacrylamide homopolymers or copolymers of these with each other and/or with acrylic or methacrylic acids, cationic monomers, or any mixtures of these.

3. A method according to Claim 2 in which the said polymers make up to 40% of the thickener.

4. A method according to Claim 3 in which the said polymers make up 25-30% of the thickener.

5. A method according to any one of Claims 2 to 4 in which the said polymers are lightly cross-linked by incorporation of 0.1 to 5% by weight of a di- or poly-functional olefinically unsaturated compound.

6. A method according to any one of Claims 2 to 5 in which an inversion surfactant is added to the thickener.

7. A thickener for aqueous based compositions which is a water in oil emulsion.

8. A thickener according to Claim 7 in which the water phase of the emulsion contains water soluble polyacrylamide or polymethacrylamide homopolymers or copolymers of these with each other and/or with acrylic or methacrylic acids, cationic monomers, or any mixture of these.

9. An aqueous based compound thickened by the method of any one of Claims 1 to 6.

European Patent Office

0042678

Application number
EP 81 30 2434

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	US - A - 3 849 361 (M.L. ZWEIGLE) * Column 1, lines 12-22; 37-40; column 3, lines 5-49; column 5 lines 39-42; examples 2,3; claims 1-7 * --	1,2,6-8	C 09 D 7/00 C 08 J 3/02 C 09 K 7/00 C 08 L 33/00 C 09 D 5/00
X	US - A - 3 734 873 (D.R. ANDERSON) * Column 1, lines 27-35; 58-67; column 2, lines 1,2, 27-54; column 4, lines 52-62; claims 1-13 * --	1-3,5-8	TECHNICAL FIELDS SEARCHED (Int. Cl.³)
X	US - E - 28 474 (D.R. ANDERSON) * Column 1, lines 12-21, 45-57; column 2, lines 1-10, 20-25, 42-49; column 4, lines 62-67; claims 1-19 * --	1-3,6-8	C 09 K 7/00 7/02 C 09 D 7/00 C 08 J 3/02
	US - A - 4 022 736 (J.M. SCHMITT) * Column 1, lines 1-19; claims 1-9 * --	1,2,6-8	
	US - A - 3 867 330 (A.J. FRISQUE) * Column 1, lines 1-25; column 5, lines 54-67; column 6, lines 1-10; claims 1-5 * --	1,2,7,8	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document
	GB - A - 2 017 159 (ALLIED COLLOIDS) * Page 1, lines 27-64; page 2, lines 4-13 * ----	1,2,5-9	T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document